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REFRIGERATION LUBRICANT BASED ON POLYOLESTER FOR USE WITH HFCS AND PROSPECT OF ITS APPLICATION WITH R-22 (PART 1) TRIBOLOGICAL CHARACTERISTICS

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ABSTRACT

Tribological behavior was evaluated for polyolester base oil and the formulated oils in some HFCs and HCFC refrigerants environment. HFCs as well as R-22 showed the boundary lubricating effect depending upon the solubility of gas in the oil. Thus, higher gas pressure of the refrigerants improved the wear resistance. A synergistic effect on antiwear properties was found when using an aryl phosphate together with a sulfur-phosphorus type additive whose performance was comparable to that with the formulated alkylbenzene in R-22. The surface analysis showed that the improvement of antiwear performance was because of promoting the formation of a reaction film containing both iron phosphate from aryl phosphate and the decomposition products of polyolester on the sliding surfaces.

INTRODUCTION

In accordance with the predetermined schedules of the international treaty based upon Montreal protocol, the production of chlorofluorocarbons (CFCs) was totally banned by the end of year 1995 and that of the hydrochlorofluorocarbons (HCFCs) has been phased out to meet future regulatory legislation requirements. Instead, hydroflourocarbons (HFCs) having no ozone depleting potential have been regarded as alternative refrigerants. Since the replacement of CFCs seems to have been successfully completed in household refrigerators and automotive air conditioners, the current major concern is application of HFCs to air conditioners and low temperature refrigeration equipments. In refrigeration compressor applications, one of the key issues is the lubricant performances which are primarily miscibility with HFCs, thermal and chemical stability and tribological properties. Polyolesters (POEs) have been regarded as one of the most prominent candidates of refrigeration lubricant for HFCs. However, it has been pointed out that POE has the drawback of hydrolysis which results in sludge formation and wear enhancement in compressors [1]. Thus, POE lubricants have to be optimized from a viewpoint of chemical structure of base oil and the additive formulations. The present paper describes the tribological performance of the developed refrigeration lubricant based upon a specified combination of POE and the additive packages.

OILS TESTED AND SOLUBILITY OF OIL/REFRIGERANT MIXTURE

The base oils of lubricants tested are a pentaerythritol type ester POE(A32) and an alkylbenzene AB having a branched alkyl substituent. Some properties of base oils and compositions of additive-containing POEs are listed in Tables 1 and 2, respectively. All the formulated POEs contain in common a small amount of a phenol type antioxidant and an epoxide type stabilizer whose performance is described in part 2 report. In addition, an aryl phosphate (AP) and a sulfur-phosphorus (S-P) type antiwear additive were separately or together added to improve the wear resistance, in which POE-C contained as much AP as POE-A and as much S-P as POE-B.

First, the viscosity of oil/refrigerant mixture was measured with a falling piston type viscometer as shown in Fig.1. Figure 2 shows the viscosity as well as the solubility of refrigerant gas in the oil under a constant gas pressure and temperature. The oil/refrigerant mixture showed the lower viscosity than the oil in the air for each oil. Decline of viscosity of POE with refrigerant was more significant for R-22 than for HFCs, and the viscosity of POE/HFC was

in the order of R-404A > R-407C > R-134a. This order is the opposite to that of observed solubility of refrigerant in POE as shown in the figure. On the other hand, when compared between POE and AB for R-22, the viscosity of POE decreased more significantly than that of AB. These indicate that the viscosity of the oil in the presence of refrigerant is governed by the solubility of gas in the oil.

TRIBOMETER AND TESTING CONDITIONS

The experimental apparatus for friction and wear test was a block-on-ring type tribometer. The ring and the block are made of nickel chromium molybdenum steel (SAE4620) and alloy tool steel (SAE01), respectively. They were machined and heat treated to a hardness HRC 58-62 for the ring and HRC 28-32 for the block. The ring was 35mm in outer diameter and 8.7mm in width, and the block was 6.35mm in width. The surfaces of both the test specimens were ground to the initial surface roughnesses less than R_a of 0.2 μ m.

After the test chamber was evacuated, refrigerant gas was charged up to the required pressure. Then, the test was started under a predetermined load and the initial bulk temperature. During the test both the frictional force and bulk temperature were recorded on a personal computer. After the test, the specific wear rate was determined based on the width of the wear scar on the block and the wear loss of the ring. The experiments were carried out under the sliding speed of 0.5m/s, the initial bulk temperature of 80℃ and the load in the range from 750N(76.5kg) to 1250N(127.5kg) for the test duration of 60 minutes.

EFFECT OF REFRIGERANTS

Figure 3 shows the frictional characteristics of POE base oil determined varying gas pressure. Under the gas pressure of 100kPa(1.0kg/cm^2), the coefficient of friction abruptly increased to reach the seizure before the end of the run. When elevating gas pressure up to 200kPa(2.0kg/cm^2), the coefficient of friction became steady state during the run. Meanwhile, the coefficient of friction under the highest gas pressure continued to decrease until the end of run. It is apparent that the increase in gas pressure prevented seizure and reduced the coefficient of friction.

The specific wear rate for POE base oil varying the refrigerants is given in Fig.4. The combination of POE/R-22 showed much lower wear rate than POE/HFCs. On the other hand, the wear rate with R-404A was the highest of the data in HFCs, R-407C the intermediate and R-134a the lowest. The order of antiwear performance with refrigerant agrees well with that of solubility of refrigerant in POE as shown in Fig.2. It implies that antiwear performance of POE base oil may be correlated with the solubility of refrigerant in the oil.

EFFECT OF ADDITIVES

Figure 5 compares the antiwear properties of the formulated oils listed in table 2 in R-134a environment. The wear rate increased consistently with load for each oil. All the formulated POEs showed the low wear rate compared with that for POE base oil under the loads from 750N(76.5kg) to 1000N(102kg), in which POE-C containing both AP and S-P was superior to both POE-A and POE-B. Under the highest load of the present experimental conditions, however, both POE-A and POE-B became almost ineffective while POE-C remained its effect whose wear rate was almost equal to that for the formulated AB-A in R-22. That is, a synergistic effect of the additives on wear resistance was found when using AP together with S-P type additive.

Wear behavior of the formulated POEs was compared varying refrigerant under the highest load condition as shown in Fig.6. As is evident in the figure, POE-C shows the highest wear resistance of the POEs in each refrigerant. On the other hand, when comparing between the data obtained varying refrigerant for each additive-containing POE, it is common to the results for all the POEs that the wear rate in R-134a is the highest, R-407C the intermediate and R-404A the lowest. That is, the variation in wear rate with refrigerant for the additive-containing POEs is contrary to that obtained for POE base oil in Fig.4. As shown earlier, the wear rate for POE base oil was considerably influenced by the amount of dissolved refrigerant in the oil. Thus, this contradictory result implies that a competitive adsorption

between refrigerant and additives occurred on the sliding surfaces in the case of formulated POEs.

SURFACE OBSERVATION AND SURFACE ANALYSIS

Figure 7 shows the surface observation of rings by means of an optical microscope. It is observed that there are some parts similar to the block material on the surface for POE-A, meanwhile the surface for POE-C is generally smooth. It is inferred that adhesion occurred on the sliding surfaces which resulted in transfer of the mating material to the ring surface.

The surfaces of rings were analyzed by X-ray photoelectron spectroscopy (XPS). Figure 8 shows the XPS spectra of the detected elements, and table 3 summarizes their atomic concentrations at the outermost surfaces. In F1s spectra shown in Fig.8(a), the binding energy (B.E.) at the peak is the same for all the results, which indicates the presence of FeF_2. The atomic concentration of F is in the order of POE-A > POE-B > POE-C. The peak at B.E. in P2p spectra, which is common to the results for all the POEs, is ascribed to $FePO_4$. The atomic concentration of P for POE-C is approximately three times as high as those for both POE-A and POE-B as shown in table 3. This tendency is almost opposite to the results obtained with F element. Meanwhile, C1s spectrum for POE-C is appreciably different from those with the other POEs. That is, the intensity in the range of B.E. from 286 to 290eV, which is due to a chemical bond of C and O such as carbonyl, carboxylic and ether group, is higher for POE-C than for the others. This indicates that the concentration of the decomposition and reaction products of ester base oil in the film is higher for POE-C than for the other POEs. The peak at B.E. of 529.0eV in O1s spectra is due to FeO_x while the range from 530 to 533eV is ascribed to oxygen having a chemical bond with carbon. POE-C shows much lower intensity of FeO_x but higher intensity of C-O than both POE-A and POE-B, which reasonably agrees with the results in C1s spectra.

DISCUSSION

From these results, it may be concluded that the refrigerants play an important role in boundary lubrication depending upon the solubility of gas in the oil when lubricated with POE base oil in R-22 and HFCs. On the other hand, there must be a competitive adsorption accompanying a reaction film between refrigerant and antiwear additives on the sliding surfaces when the formulated POEs are used, in which the effect of additives is predominant. S-P type additive has a role of promoting formation of iron phosphate derived from aryl phosphate and iron soap from ester base oil on the surfaces. With respect to the mechanism of wear reduction based on the interaction between the two additives, further study would be required.

CONCLUSIONS

Friction and wear performances of polyolesters with and without additives were studied with a block on ring type tribometer in some HFCs and R-22 refrigerants environment. The results obtained are as follows.

(1) HFC refrigerants play a boundary lubrication role on the basis of formation of metal fluoride depending upon the solubility of gas in the oil which effectively prevents adhesion and reduces wear amount.

(2) Addition of aryl phosphate together with S-P antiwear additive in POE is beneficial for antiwear performance which is almost comparable to that for the formulated alkylbenzene in R-22.

(3) When additive-containing oils are used, there must be a competitive adsorption between refrigerant and additives onto the sliding surface.

REFERENCE

[1] Muraki M. : Proc. Int. Sym. on R-22 & R-502 Alter. Ref., Japan 1994, 101.

Table 1 Properties of base oils

	POE (A32)	AB
Structure	polyolester	alkylbenzene
Viscosity, mm^2/s		
@40°C	30.62	30.97
@80°C	8.244	6.966
Viscosity index	101	-39
LCST [1], °C		
with R-134a	-39	—
with R-407	-31	—
with R-404A	<-60	—
with R-22	<-60	<-60

1) Lower Critical Solubility Temperature

Table 2 Compositions of formulated oils

	POE-A	POE-B	POE-C	AB-A
Base oil	POE (A32)	←	←	AB
Additive				
AO[1]	O	O	O	—
Epoxide	O	O	O	O
AP [2]	O	—	O	O
S-P [3]	—	O	O	—

1) Antioxidant 2) Aryl phosphate
3) Sulfur-phosphorus type additive

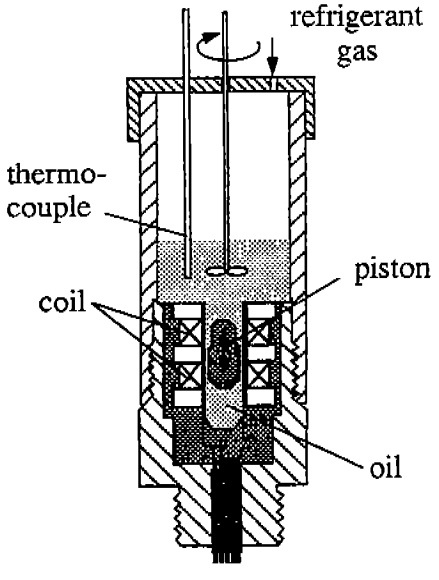


Fig.1 Falling piston type viscometer

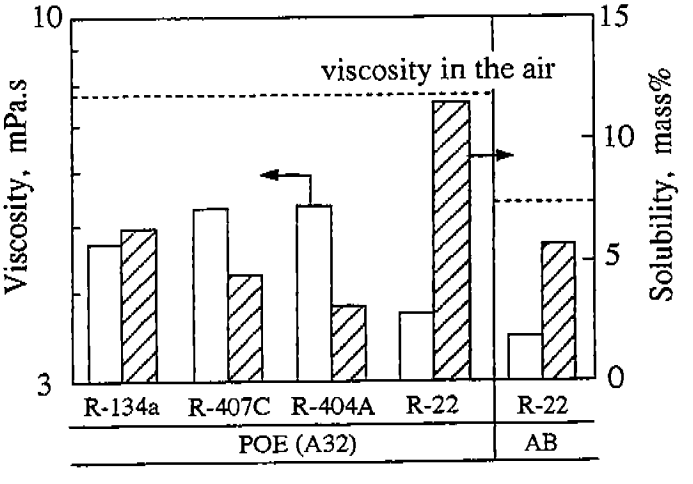


Fig.2 Viscosity and solubility of oil/refrigerant mixture
(Temp.: 80°C, Gas Pres.: 600kPa(6.0kg/cm [2]))

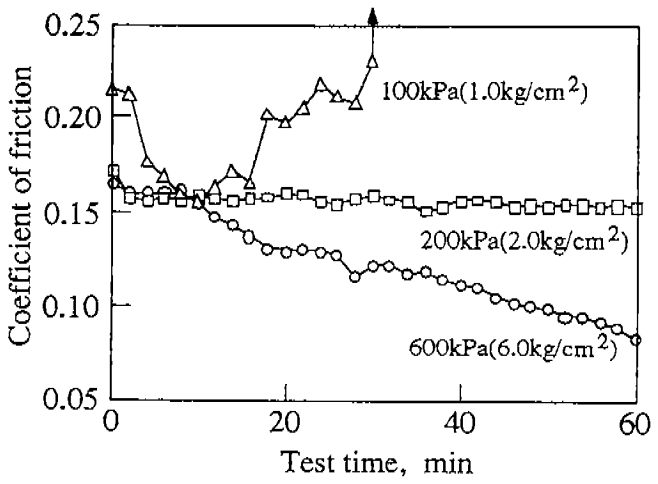


Fig.3 Frictional characteristics of POE (A32)
(Ref.: R-134a, Load: 750N(76.5kg))

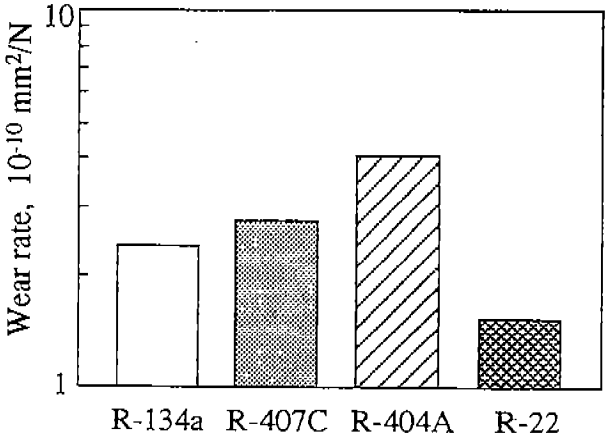


Fig.4 Antiwear properties of POE (A32)
(Gas pres.: 600kPa(6.0kg/cm 2), Load : 750N(76.5kg))

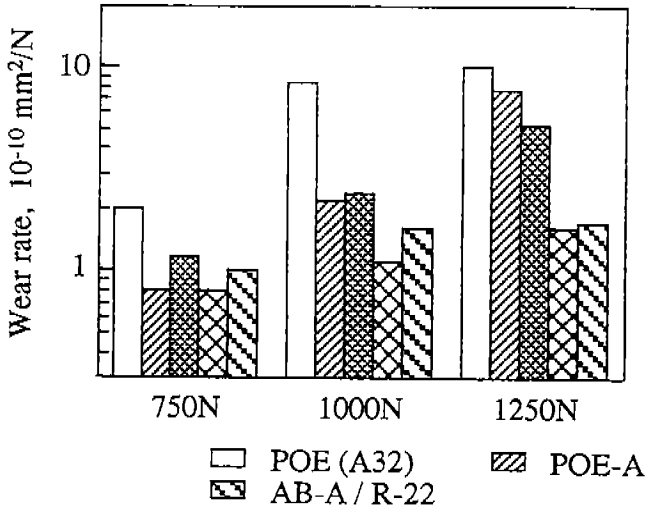


Fig.5 Wear rate for formulated oils vs load
(Ref.: R-134a, Gas pres.: 600kPa(6.0kg/cm 2))

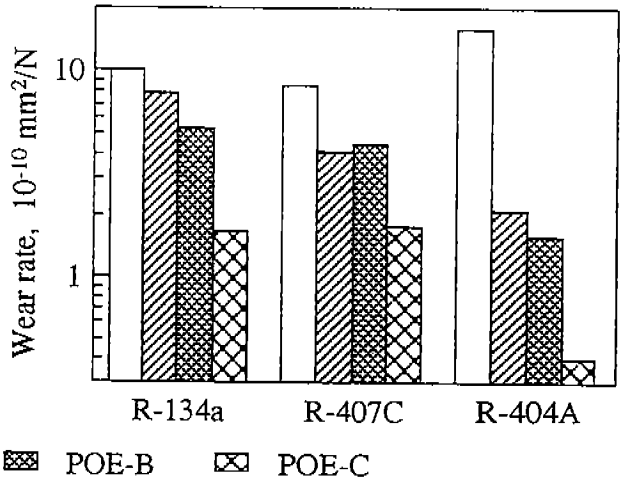
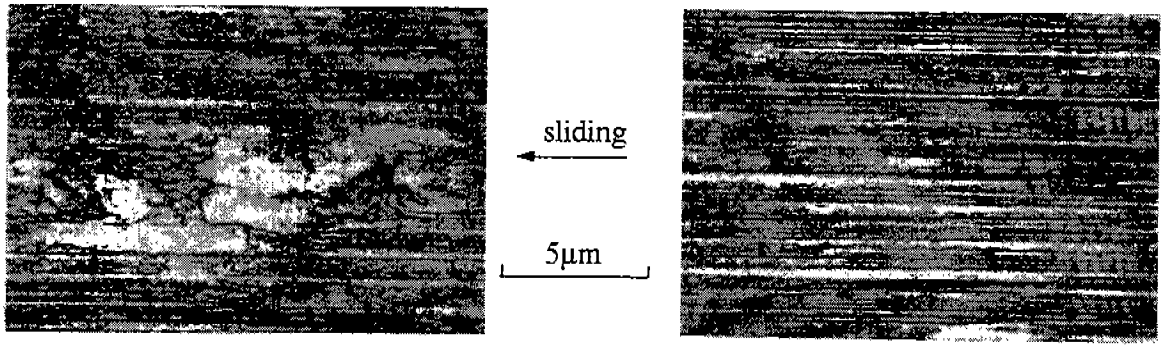


Fig.6 Antiwear properties in HFC refrigerants
(Gas pres.: 600kPa(6.0kg/cm 2), Load: 1250N(127.5kg))



(a) POE-A

(b) POE-C

Fig.7 Sliding surfaces of rings after the test
(Ref.: R-134a, Gas pres.: 600kPa(6.0kg/cm 2), Load: 1250N (127.5kg))

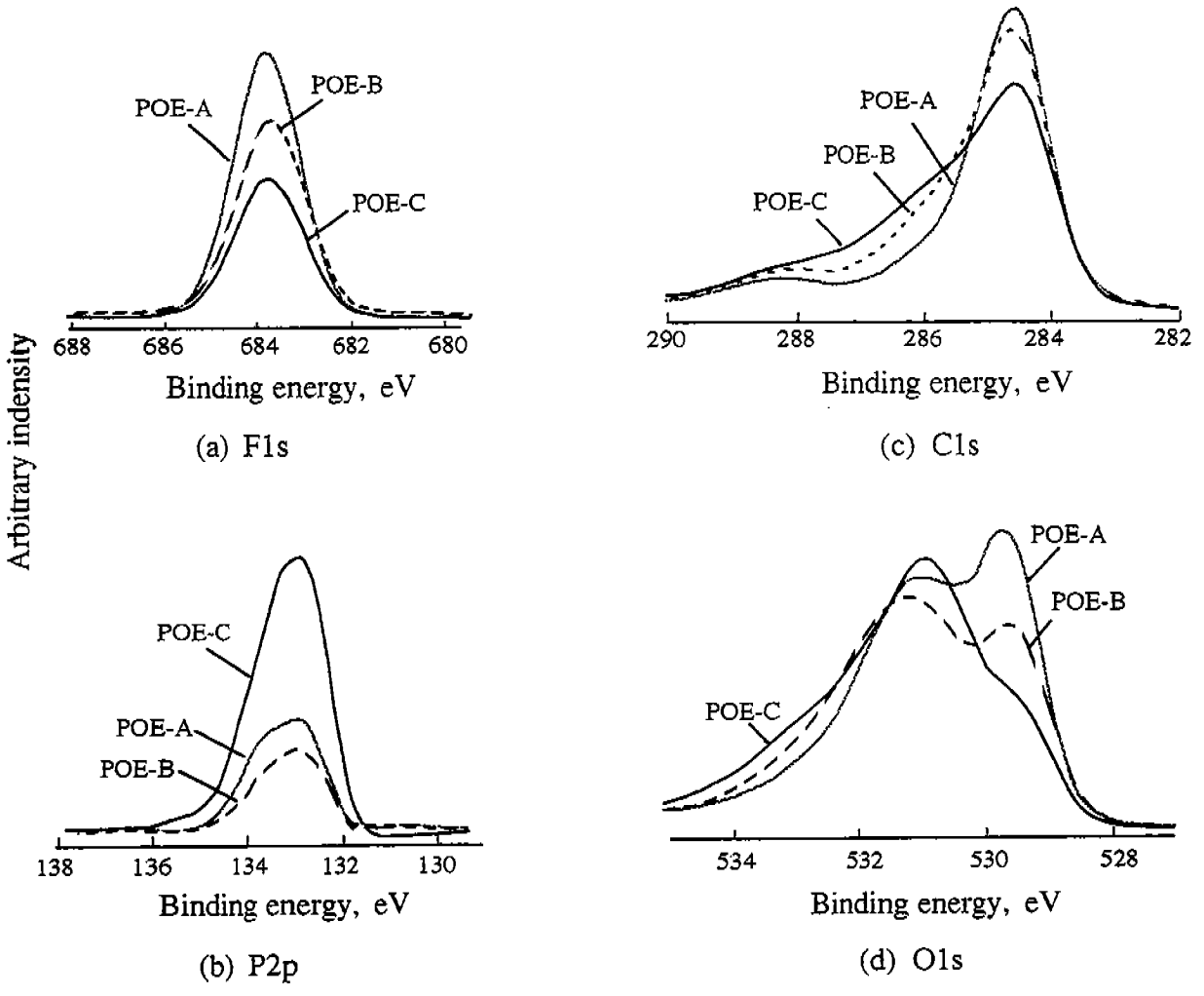


Fig.8 XPS spectra for sliding surfaces of rings with POEs
(Ref.: R-134a, Gas pres.: 600kPa(6.0kg/cm ^{2}), Load: 1250N (127.6kg))

	POE-A	POE-B	POE-C
Fe	11.68	8.48	7.70
O	34.78	31.88	33.03
C	51.80	57.92	56.05
F	0.72	0.51	0.32
P	1.02	0.81	2.90
S	—	0.40	—

Table 3 Atomic concentrations of detected elements at outermost surface
(Ref.: R-134a, Gas pres.: 600kPa(6.0kg/cm ^{2}), Load: 1250N(127.6kg))